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ABSTRACT

Absorption peaks appear in the near ultraviolet spectrum of aqueous solutions containing azide and palladium (II), unlike the case in the visible region. The existence of 5:1 and 6:1 N_3^- to Pd^{+2} complexes is indicated, in addition to the lower ratio complexes which have been reported by others. The precipitate which is sometimes formed on adding azide to a palladium (II) solution has been identified as $Pd(N_3)_2$ and some of its properties are reported.

Studies in the visible region of the spectrum on azide complexes of palladium (II) have been reported[1] to show the formation of $[Pd(N_3)_2Cl_2]^{-2}$ and the probable formation of 1:1 and 4:1 N_3^- to Pd^{+2} species in aqueous solutions and of the 4:1 species in water-acetone mixtures. The presence of $PdCl_5^{-3}$ in hydrochloric acid, as indicated by absorption spectra,[2] suggests the possibility of azide complexes in which palladium (II) has coordination numbers higher than four. Evidence for the view that four-coordinated square complexes tend to add ligands to form five- and six-coordinated systems has been summarized and discussed recently,[3] including evidence for a six-coordinated palladium (II) species in the solid state, but not in solution. However, nickel (II), the fourth period analogue of palladium (II), apparently exhibits a coordination number of six in solution. Complexes of nickel (II) containing three moles of o-phenanthroline or of ethylenediamine for one mole of nickel, as reported by Vosburgh and Cooper[4] are good examples of this.

Spectrophotometric investigations have been made in this laboratory of the azide complexes of palladium (II) in the near ultraviolet region of the spectrum. These studies indicate that, in addition to the species which have been found,[1] there may also be 5:1 and 6:1 azide to palladium (II) complexes in solution. These two have been studied in ethanol, rather than in acetone, because of the strong absorption by acetone in the ultraviolet region. Sherif and Michail[1] also found that a precipitate was sometimes formed from solutions containing palladium (II) and azide. The red-brown material has now been identified as $Pd(N_3)_2$, possibly hydrated, and some of its properties have been noted.

EXPERIMENTAL

Weighed palladium metal, for the spectrophotometric studies, was dis-

solved in aqua regia and boiled with repeated addition of concentrated

hydrochloric acid until no test for nitrate was found with brucine.[5]

It was necessary to rid the solution of nitrate because of the strong

absorption by this ion in the ultraviolet region of the spectrum. The

solution was diluted with distilled water to give a stock solution 0.1 $\underline{M}$

in Pd (II) and 0.16 $\underline{M}$ in hydrochloric acid. The concentration of this

solution was checked gravimetrically by precipitation of the palladium

with dimethylglyoxime. A 0.01 $\underline{M}$ solution of Pd (II) in approximately

1 $\underline{M}$ perchloric acid was prepared by dissolving weighed palladium metal

in red fuming nitric acid and boiling with perchloric acid until a neg-

ative test for nitrate was found. This solution was used only in the

preparation of the palladium azide.

Stock solutions of sodium azide 0.1 $\underline{M}$ in water and 0.01 $\underline{M}$ in

commercial absolute ethanol were prepared from sodium azide, the purity

of which had been determined by the silver-thiocyanate (Volhard) method.

The absence of interfering halides in this determination was shown with

silver nitrate after destroying a sample of azide with sodium nitrite in

a solution acidified with perchloric acid. A Beckman model DU spectro-

photometer was used with matched quartz cells for all absorption meas-

urements. Blank solutions contained all ingredients except azide.

Palladium azide was prepared by adding 0.1 $\underline{M}$ sodium azide to

0.01 $\underline{M}$ palladium perchlorate in stoichiometric ratio. The precipitate

was washed with water to a pH of 4.0 and the ratio of azide to palladi-

um was determined on the moist product because it could not be dried

without exploding. Swabs of the precipitate containing 0.3-0.8 mg.

of palladium were taken on quartz wool and heated very slowly in vac-
uum from 20° to 300°. The nitrogen evolved was measured and the number
of moles calculated.[*] The palladium metal left on the quartz wool was
dissolved in aqua regia and determined spectrophotometrically with 2-
nitroso-1-naphthol.[6] The ratio of azide to palladium was found to
be 1.9:1. A similar precipitate, formed on long standing from a pal-
ladium chloride solution, gave a negative test for chloride after the
azide had been destroyed with nitrous acid. It was not possible to
determine water crystallization by difference as it was
necessary to carry out the analysis on the moist precipitate. Even
with this precaution two samples were lost by explosion during the
analysis for nitrogen.

RESULTS

Palladium Azide

Sherif and Michail[1] have noted the slow formation of a gelat-
inous precipitate when palladium and azide react in the presence of
chloride but they have given no indication of the composition of the
precipitate, which might contain chloride or hydroxide in addition to
azide. It was found in the present work that the precipitate forms
immediately from a palladium perchlorate solution, containing no chlor-
ide, when the ratio of azide to palladium is 2 to 1 or less. The pro-
duct, shown above to be $Pd(N_3)_2$, dissolves in excess azide, in a large

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[*]The nitrogen determination was made by V. H. Tashinian, University of
California microchemical analytical laboratory.

excess of chloride or in ammonia. It is explosive when dry and may contain water of hydration which would not be shown by the method of analysis.

A flaky crystalline form of the azide was obtained on one occasion when a solution of 3×10^{-5} $\underline{M}$ Pd^{+2} and 1×10^{-3} $\underline{M}$ N_3^- had stood for two weeks at pH 6.5. Attempts to obtain X-ray diffraction powder patterns of moist palladium azide resulted in decomposition of the material. The patterns of the palladium metal formed showed only broad diffuse rings, indicating a very small particle size.[*]

Absorption Spectra

As the azide to palladium ratio is increased from 4:1 to 10:1 in aqueous solution the absorption spectra from 290 mμ to 350 mμ exhibit peaks which shift to longer wave lengths (Fig. 1). At ratios higher than 10:1 the peak absorbances remain at 315 mμ although the maximum absorbance is not shown until a ratio of 150:1 for N_3^- to Pd^{+2} is attained. The molar absorptivity coefficient, based on the palladium content, is 18,300 at this ratio. The tetraazido palladium (II) complex has been shown to exist in aqueous solution[1] and the shift in wavelength of the peaks is probably explained by the conversion of all of the $[Pd(N_3)_2 Cl_2]^{-2}$ species to $Pd(N_3)_4^{-2}$. At a pH of 2-3 essentially all of the color of the aqueous solutions can be extracted into an equal volume of n-butyl alcohol or isoamyl alcohol, though none is extracted at pH 6.5.

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[*]The X-ray patterns were obtained by Helena Ruben and G M. Gordon.

The absorption curve shown in Fig. 1 for a ratio of 4:1 N_3^- to Pd^{+2} in ethanol exhibits a peak at the same wave length as do the curves for all ratios from 3:1 to 7:1 in ethanol for either 10^{-3} $\underline{M}$ or 10^{-5} $\underline{M}$ palladium (II).

Composition of Complexes in Ethanol

Application of the molar ratio method of Yoe and Jones[7] to solutions in ethanol over the concentration range from 5×10^{-5} $\underline{M}$ to 1×10^{-3} $\underline{M}$ Pd^{+2}, containing 0.05% to 1.0% water by volume, gives sharp breaks in the curves indicative of the formation of five- and six-coordinate complexes, as shown in Fig. 2. The six-coordinate palladium (II) break first appears on increasing the concentration to 1×10^{-3} $\underline{M}$ Pd^{+2}, and appears only between 300 mμ and 340 mμ. Below this concentration, which is near the spectrophotometric limit of study in 0.1 cm. cells, only the five-coordinate break appears.

It is likely that the tetrachloro and tetraazido complexes of palladium (II) exist in solution as six-coordinate complexes with molecules of solvent filling two of the positions.[3,8] Although it is clear that all chloride ions and solvent molecules have been displaced when six azides have been added it is not certain that pentaazido and hexaazido complexes have been formed at the corresponding breaks. Pearson and Basolo have shown that chloride in some cobalt (III) complexes can be replaced with hydroxide, even in acid solutions where the hydroxide ion concentration is very low.[9] They have further inferred that azide may undergo methanolysis with similar subsequent reactions between cobalt (III) complexes and methoxide.[10]

The results presented here were obtained in unbuffered solutions because there appeared to be no suitable buffer for palladium in alcohol (e.g., acetate appears to complex palladium). As the sodium azide concentration is increased the solution becomes more basic and the hydroxide and ethoxide ion concentrations increase. In view of the apparent reactions for cobalt complexes with hydroxide and methoxide ions, similar reactions of the palladium complexes with one or more hydroxide or ethoxide ions should be considered. The results presented only show the ratios of ligand to metal and the question of hydrolysis or ethanolysis is open to further investigation.

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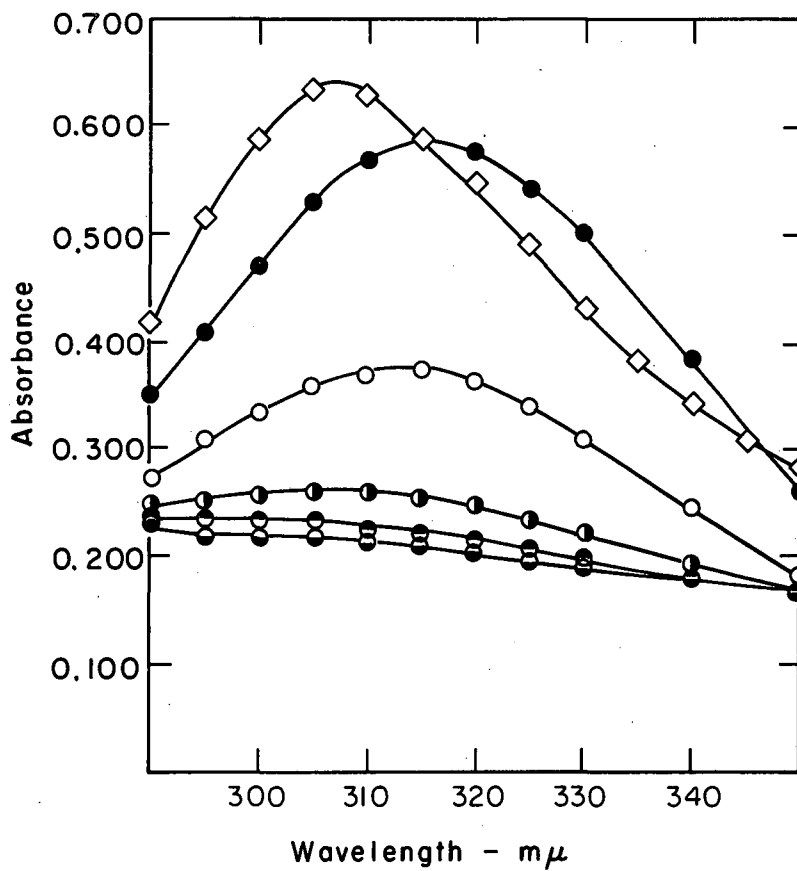   5379 (1957); ibid, 79, 5382 (1957).

FIGURE CAPTIONS

Figure 1. ◇ 1×10^{-3} $\underline{M}$ Pd^{+2} and 4×10^{-3} $\underline{M}$ N_3^- in 99.0 percent ethanol

◒ 4×10^{-4} $\underline{M}$ Pd^{+2} and 16×10^{-4} $\underline{M}$ N_3^- in water

◓ 4×10^{-4} $\underline{M}$ Pd^{+2} and 24×10^{-4} $\underline{M}$ N_3^- in water

◑ 4×10^{-4} $\underline{M}$ Pd^{+2} and 28×10^{-4} $\underline{M}$ N_3^- in water

◯ 4×10^{-4} $\underline{M}$ Pd^{+2} and 40×10^{-4} $\underline{M}$ N_3^- in water

● 4×10^{-4} $\underline{M}$ Pd^{+2} and 60×10^{-4} $\underline{M}$ N_3^- in water

All measurements made in 0.1 cm. cells.

Figure 2. ◯ 1×10^{-3} $\underline{M}$ Pd^{+2}; $\lambda = 300$ mμ; 0.1 cm. cell

◓ 1×10^{-3} $\underline{M}$ Pd^{+2}; $\lambda = 340$ mμ; 0.1 cm. cell

◒ 5×10^{-5} $\underline{M}$ Pd^{+2}; $\lambda = 300$ mμ; 1.0 cm. cell

● 5×10^{-5} $\underline{M}$ Pd^{+2}; $\lambda = 340$ mμ; 1.0 cm. cell

The 1×10^{-3} $\underline{M}$ Pd^{+2} solution contains one percent water

by volume from dilution of the stock palladium solution

and the 5×10^{-5} $\underline{M}$ Pd^{+2} solution contains 0.05 percent

water.

Fig. 1

Fig. 2

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